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RAIN REPELLENT

28 DECEMBER 1962

Prepared under
Navy, Bureau of Naval Weapons

CONTRACT NOw 62-0557-c
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Covering Period
21 September 1962 through 20 December 1962

FOSTER D. SNELL, INC.

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ABSTRACT

Stability in storage was found to be greater for the silicone-titanium copolymer alone or in solution in mineral spirits than with combinations of silicone-titanium copolymer and dimethyldiethoxysilane.

A saturated solution of p-toluene sulfonic acid was found effective as a catalyst for the silicone-titanium copolymer alone and in solution in mineral spirits when applied to a dry panel in pre-flight application. Its stability on storage was found to be greater than that of sodium bisulfate in paste form.

A re-evaluation was made of several surface active agents incorporated in acidified dimethyldiethoxysilane. Instead of quick release at 40 psi. pressure, as previously used, a gradual release at 5 psi. pressure at a rate of 1 milliliter per minute for 10 minutes was employed. No significant improvement in repellency was obtained when application was made under rain conditions.

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I. INTRODUCTION

During the preceding quarter it was established that a combination of silicone-titanium copolymer and dimethyldiethoxysilane was effective both when applied in continuous stream under rain conditions and when applied in conjunction with a sodium bisulfate paste on a dry panel. On storage, however, the combination of silicone-titanium copolymer and dimethyldiethoxysilane lost effectiveness. The explanation appears to lie in the reaction under storage conditions between the dimethyldiethoxysilane and the residual alkoxy groups in the copolymer to form a more highly cross-linked polymer. The silicone-titanium copolymer alone and the silicone-titanium copolymer in solution in mineral spirits were effective when applied during rain conditions and they were found to retain their effectiveness after storage. The reason for the use of the combination of silicone-titanium copolymer and of the dimethyldiethoxysilane was that with the aid of the sodium bisulfate catalyst, a rain repellent film could be obtained on a dry panel under pre-flight conditions. Investigation was therefore undertaken to obtain a suitable catalyst for the silicone-titanium copolymer without combination with dimethyldiethoxysilane which would give a rain repellent film on a dry panel.

In continuation of work carried out during the preceding quarter further investigation was made of the use of Tyzor "PB" (partially polymerized tetrabutyl titanate) as well as of Tyzor "TOG" (tetraoctylene glycol titanate) and Tyzor "TBT" (tetrabutyl titanate) in preparation of silicone-titanium copolymers.

The sodium bisulfate paste, which was established to be effective for use on a dry panel in conjunction with the silicone-titanium copolymer and dimethyldiethoxysilane combination, was found to lack stability on storage. Investigation was therefore undertaken to find a catalyst which would retain its usefulness after storage. This became an additional requirement of the catalysts under investigation for use with the silicone-titanium copolymer without combination with dimethyldiethoxysilane.

A re-evaluation of surface active agents in conjunction with acidified dimethyldiethoxysilane was made. In our study of surface active agents incorporated in acidified dimethyldiethoxysilane, which was made in the first quarter under the present contract, 10 milliliters of repellent were sprayed through the repellent outlet of our rain spray apparatus onto the test panel in a continuous stream at a pressure of 40 pounds per square inch, while the panel was exposed to a rainfall of 1 inch per hour per square foot at a wind speed of 175 miles per hour. During the present quarter several

surfactants incorporated in acidified dimethyldiethoxysilane were re-tested under conditions which were found useful for the deposition of repellent films with silicone-titanium copolymers. The test panel was exposed to the normal test conditions of 3 inches of rainfall per hour per square foot at a wind speed of 290 miles per hour. The repellents were released into the windstream at a pressure of 5 pounds per square inch and a rate of 1 milliliter per minute for 10 minutes.

II. SILICONE-TITANIUM FORMULATIONS

A. PREPARATION OF SILICONE-TITANIUM COPOLYMERS.

The preparation of silicone-titanium copolymers was continued during the present quarter. Copolymers of dimethyldiethoxysilane hydrolysate with tetrabutyl titanate and with partially polymerized tetrabutyl titanate were prepared.

Copolymer P.

To 100 milliliters of dimethyldiethoxysilane, containing 0.25 milliliter of concentrated sulfuric acid, 50 milliliters of water were added slowly with stirring. An exothermic reaction occurred and on continued addition of water a silicone oil phase separated. After addition of all of the water 25 milliliters of a 4 per cent solution of sodium carbonate in water were added to neutralize the acid catalyst. The oil layer was extracted with 50 milliliters of hexane and the hexane solution of the hydrolysate was heated to a pot temperature of 100-105°C. and hexane, ethanol and water removed by distillation. Fifty milliliters of hydrolysis product were obtained as a residue.

To 50 milliliters of hydrolysis product were added 5 milliliters of partially polymerized tetrabutyl titanate, Tyzor "PB", in 20 milliliters of hexane. The reaction mixture was refluxed for 2 hours at a pot temperature of 150°C. A clear amber liquid copolymer was obtained.

Copolymer Q.

To 50 parts of hydrolysis product 3 parts of partially polymerized tetrabutyl titanate and 20 parts of hexane were added and the reaction mixture refluxed for 2 hours at a pot temperature of 150°C. A clear amber liquid copolymer, similar to Copolymer P, was obtained.

Copolymer R.

To 50 parts of hydrolysis product, obtained as described above, 25 parts of tetrabutyl titanate were added and the reaction mixture refluxed for 2 hours at a pot temperature of 200°C. A dark amber liquid copolymer was obtained.

Copolymer S.

To 50 parts of hydrolysis product were added 25 parts of tetrabutyl titanate and the reaction mixture refluxed for 2 hours at a pot temperature of 150°C. A dark amber liquid copolymer, similar to Copolymer R, was obtained.

B. EVALUATION OF SILICONE-TITANIUM FORMULATIONS.

During the preceding quarter formulations containing silicone-titanium copolymers were found to form repellent films when applied under in-flight rain conditions. Formulations containing Copolymer H and dimethyldiethoxysilane gave the desired coating action when applied in continuous stream during in-flight rain conditions and when applied to a dry panel in conjunction with a sodium bisulfate catalyst in pre-flight application. The most promising of these formulations were packaged in tin lined Spratainers made by Crown Cork & Seal Co., Inc., Chicago, Illinois with Emson Research, Inc. S-32 stainless steel valves.

Earlier attempts to apply repellents based on acidified dimethyldiethoxysilane during simulated in-flight rain conditions were unsuccessful. Aerosol packages (Formulas 2911H-2355 and 2356 (described in the Final Report dated 10 January 1962 under Contract NOw 61-0463-c) were held close to the test panel and large quantities of repellent were sprayed, but the bulk of these formulations was swept away from the surface of the glass by the high speed air-water jet hitting the panel. Some repellency was noted at the edges of the test panel on areas furthest from the point of air-water impact.

Formulas 2911K-291, 293, and 294, containing combinations of silicone-titanium Copolymer H and dimethyldiethoxysilane, were found to give the desired coating action when sprayed from aerosol packages during simulated in-flight rain conditions. Each coated 100 per cent of the panel and had a rain spray life of 2 minutes. Formula 2911K-291, which contains 20 parts silicone-titanium Copolymer H, 20 parts dimethyldiethoxysilane, and 60 parts Freon 12, was subjected to high temperature storage. After two weeks at 160°F. Formula 2911K-291 deposited a chalky white film on the panel during in-flight application.

In an effort to determine whether Copolymer H was unstable when stored at 160°F. or had reacted with dimethyldiethoxysilane, samples of Copolymer H and a 50 per cent solution of Copolymer H in dimethyldiethoxysilane were aged for one week at 160°F. No change was noted in the behavior of Copolymer H after storage. Film-forming ability under in-flight rain conditions was good and no precipitate was formed when a few drops of copolymer were added to water in the Drop Test, as described in Interim Report No. 2, dated 28 September 1962, under the present contract. The Film Test, also described in the above report, gave a clear continuous film when 1 milliliter of copolymer was floated on the surface of 125 milliliters of water contained in a 250 milliliter beaker and allowed to stand at room temperature overnight. When the aged 50 per cent solution of Copolymer H in dimethyldiethoxysilane was tested in accordance with the Drop Test, a gummy white precipitate was formed, while the Film Test resulted

in a hazy, brittle film. From the results of these qualitative tests it appears that Copolymer H is stable after one week's storage at 160°F., but that solutions of Copolymer H and dimethyldiethoxysilane react under the storage conditions. The product is probably a more highly cross-linked copolymer formed by reaction between dimethyldiethoxysilane and residual alkoxy groups in the copolymer. Subsequent high temperature storage of Formulas 2911K-290 and -379, which contain Copolymer H and a 50 per cent solution of Copolymer H in Sovasol 5, respectively, in combination with Freon 12, further indicates that Copolymer H is stable in the absence of reactive materials such as dimethyldiethoxysilane. These formulations show no decrease in film forming ability under in-flight rain conditions after a month's storage at 160°F. High temperature storage stability tests are being continued.

The instability of Copolymer H in combination with dimethyldiethoxysilane at elevated temperature resulted in the elimination of dimethyldiethoxysilane from the repellent formulation. The reason for the incorporation of dimethyldiethoxysilane in the formulation was that the dimethyldiethoxysilane could be successfully catalyzed by the sodium bisulfate paste for the pre-flight application. The elimination of dimethyldiethoxysilane would prove to be of no consequence for the in-flight application, as Formula 2911K-290, which contains 20 per cent Copolymer H, 20 per cent Sovasol 5, and 60 per cent Freon 12, coats 100 per cent of the test panel and has a rain spray life of two minutes. For the pre-flight application the elimination of

dimethyldiethoxysilane from the formulation could pose a major obstacle, as the sodium bisulfate catalyst paste will not deposit a useful repellent film when used in conjunction with Copolymer H.

Copolymer H is not stable in acid media. This is evident when we combine acidified dimethyldiethoxysilane and Copolymer H and obtain a white precipitate, a sign that Copolymer H is being decomposed. It was reasoned that although the sodium bisulfate paste does not deposit a useful film when used in conjunction with Copolymer H, there might be another acid composition that would split Copolymer H in the proper manner to form a repellent film of satisfactory life. It was determined that concentrated sulfuric acid would catalyze Copolymer H to provide a useful repellent film, when the repellent and catalyst are applied to a clean, dry panel. Copolymer H has within its composition the essentials from which a repellent film can be formed when properly catalyzed. It is believed that the concentrated sulfuric acid splits the silicone-titanium copolymer to form a silicone oil, titanium dioxide, and titanium sulfate. The silicone oil is then catalyzed by the acid to form a repellent film on the glass surface. Similar results would be obtained if the organosilicon products did not have a chance to combine to form a silicone oil, but had directly attached to the glass surface through a silylbisulfate mechanism. Regardless of the mechanism involved, Copolymer H

can be made to function properly in both applications providing the necessary catalyst is available for pre-flight application.

In Section III of this report it is stated that the sodium bisulfate paste, in addition to its inability to catalyze Copolymer H to give a film of one-hour duration, lacked stability. A p-toluene sulfonic acid formulation was developed to take the place of the sodium bisulfate paste as an answer to the stability problem. The p-toluene sulfonic acid catalyst proved to be as useful as concentrated sulfuric acid for the prupose of catalyzing Copolymer H to form a repellent film on a dry panel. With this improved catalyst there was no need of having dimethyldiethoxysilane in the repellent formulation, especially in view of the instability of the formulations containing dimethyldiethoxysilane and the silicone-titanium copolymer at elevated temperatures.

In the light of these facts, Formulas 2911K-290, 292, 379, and 381 to 390, were evaluated. In each case Copolymer H is combined with a solvent and packaged in an aerosol can using Freon 12 as the propellent. The formulations are all effective during in-flight application, coating 100 per cent of the panel and having rain spray lives of two minutes. With Formulas 2911K-292 and -381, a large quantity of repellent is needed to coat 100 per cent of the panel. These formulations contain 2 per cent and 4 per cent of Copolymer H, respectively. Formula 2911K-379, containing 40 per cent Copolymer H and 60 per cent Freon 12, is very effective in coating all of the panel when small quantities of repellent are applied. The relative disadvantage in this formulation lies in the fact that the excess repellent applied to the glass

panel does not flow or sweep across the glass surface as readily as formulations containing suitable solvents.

Formula 2911K-389 contains 20 per cent Copolymer H and 20 per cent n-butanol. Formula 2911K-390 contains 20 per cent Copolymer H and 20 per cent isopropanol (99 per cent). In each instance there is very little improvement in sweep when compared with Formula 2911K-379, although the compatibility of Copolymer H with isopropanol would prove to be an important factor if a repellent formulation is applied from an aircraft's windshield de-icer system. Formulas 2911K-290, 292, and 381 to 388 each contain Sovasol 5 as the solvent. In each case the sweep or movement of excess repellent across the panel was an improvement over the sweep with Formula 2911K-379, which contains only Copolymer H and propellent. Of these formulations the one that seems to hold the most promise is Formula 2911K-290, a combination of 20 per cent Copolymer H, 20 per cent Sovasol 5, and 60 per cent Freon 12. Formula 2911K-290 coats 100 per cent of the panel and has a rain spray life of two minutes when applied during in-flight rain conditions on the rain spray test apparatus.

Formula 2911K-290 provides a sufficient quantity of Copolymer H for ready catalysis when applied in conjunction with the p-toluene sulfonic acid catalyst in pre-flight application. It gives a repellent film having a rain spray life of one hour. Storage stability tests indicate that

Formula 2911K-290 and Formula 2911K-379, which contains only Copolymer H and Freon 12, are stable after one month's aging at 160°F. Both formulations are easily catalyzed by the p-toluene sulfonic acid catalyst, Formula 2911K-353, for pre-flight application and have good film-forming properties when applied during in-flight rain conditions.

In addition to formulations containing Copolymer H, formulations containing silicone-titanium copolymers whose preparations are described in Part A of this section were evaluated. Formulas 2911K-287 and 288, each containing Copolymer P, left an undesirable resinous formation at the edges of the panel during in-flight testing.

Formulas 2911K-354 to 378 inclusive, each contain silicone-titanium Copolymer R. Silicone-titanium Copolymer R was prepared in a manner similar to the preparation of Copolymer H, the exception being the temperature at which the tetrabutyltitanate and hydrolysis product were refluxed. Copolymer H was prepared at 100°C. while Copolymer R was prepared at 200°C. This 100°C. differential in the pot temperature gave rise to a copolymer whose properties were comparatively inferior to the properties of Copolymer H. Formulations in which Copolymer R was combined with dimethyldiethoxysilane or a dimethylsilicone oil resulted in the formation of a heavy resinous film during in-flight application. Formulations in which Copolymer R was utilized without an additive or when combined with a mineral spirits solvent, resulted in a repellent which had a poor sweep across the panel during in-flight application and the formation of a film having poor clarity.

Silicone-titanium Copolymer S was also prepared in a manner similar to the preparation of Copolymer H, the difference being that the pot temperature for reacting the tetrabutyltitanate and hydrolysis product was 150°C. rather than 100°C. This 50°C. differential in temperature gave rise to a copolymer, which, when tested in Formula 2911K-380, proved to have poor sweep across the panel during in-flight application and formed a film having poor clarity. With formulations containing Copolymers R and S it was anticipated that better stability on subsequent high temperature storage might be obtained as a result of the copolymer formation at higher temperatures. This sought-for improvement was not determined in the light of the poor initial properties of Copolymers R and S in comparison to Copolymer H.

Since it was found that repellent films can be applied from aerosol packages during in-flight conditions, several titanium esters were utilized in formulating aerosol packaged repellents and were evaluated. The titanium esters used were those that have in the past demonstrated their ability to form transient repellent films during in-flight application. Formulas 2911K-295 and 296, containing Tyzor "TOG" (tetraoctylene glycol titanate), Formulas 2911K-297 and 298, containing Tyzor "TBT" (tetrabutyltitanate), and Formulas 2911K-299 and 335, containing Tyzor "PB" (partially polymerized tetrabutyltitanate), formed chalky films when applied from an aerosol container during in-flight conditions.

III. PASTE AND LIQUID CATALYSTS

During the second quarter of the current contract sodium bisulfate paste compositions were prepared and found to be useful catalysts for formulations containing silicone-titanium Copolymer H and dimethyldiethoxysilane. When Formula 2911K-291, containing 20 per cent Copolymer H, 20 per cent dimethyldiethoxysilane and 60 per cent Freon 12, was applied to a clean dry panel and catalyzed by Formula 2911K-333, composed of 71.4 per cent sodium bisulfate, 14.3 per cent ethylene glycol and 14.3 per cent water, the resulting films had rain spray lives of one hour. Formula 2911K-333, which contains the aforementioned paste composition heat sealed in a polyethylene-aluminum packet, was evaluated over a period of weeks in order that the room temperature storage stability of the system might be established.

These repeated evaluations of Formula 2911K-333 in conjunction with Formula 2911K-291, led to the conclusion that Formula 2911K-333 lacks stability. Repellent films formed when utilizing Formula 2911K-291 in conjunction with Formula 2911K-333, after one week's storage, had rain spray lives which varied between 15 minutes and one hour. After two weeks' storage the combined system gave repellent films which had rain spray lives that averaged 15 minutes. In order to determine the cause of the instability of Formula 2911K-333 additional formulations based on sodium bisulfate were evaluated.

The use of Formulas 2911K-336, composed of 71.4 per cent sodium bisulfate crystals and 28.6 per cent ethylene glycol, and Formula 2911K-337, composed of 71.4 per cent sodium bisulfate powder and 28.6 per cent ethylene glycol, resulted in films having a rain spray life of 15 minutes. The use of Formula 2911K-338, a combination of 71.4 per cent sodium bisulfate powder, 25.7 per cent ethylene glycol and 2.9 per cent water, resulted in a film having a rain spray life of 15 minutes. Formula 2911K-343, composed of 71.4 per cent sodium bisulfate, 17.9 per cent ethylene glycol and 10.7 per cent water, was found to increase the rain spray life to a period of 30 minutes. The use of Formula 2911K-342, composed of 71.4 per cent sodium bisulfate powder and 28.6 per cent water, resulted in a film having a rain spray life of one hour. From the above results it was concluded that the elimination of ethylene glycol from the catalytic paste formulation would result in a much greater stabilization of the system.

A paste composed of sodium bisulfate and water has the tendency to separate after a short period of time. The utilization of ethylene glycol in the formulation decreases this separation and makes for an easier re-mixing of solids in liquid. After eliminating ethylene glycol from the paste formulation for stability reasons, additional fluids were evaluated for possible use in reducing the separation of sodium bisulfate from the liquid phase. Formula 2911K-339 made use of 28.6 per cent hexylene glycol with 71.4 per cent sodium bisulfate crystals and Formula 2911K-340 made use of 37.5 per cent hexylene glycol with 62.5 per cent

sodium bisulfate powder. In each case the paste composition was not stable, as evidenced by the decomposition of the hexylene glycol. Formula 2911K-341, composed of 57.1 per cent sodium bisulfate powder in 42.9 per cent 200 cs. dimethyl-silicone oil, proved to be of no value as the film it helped form had a negligible rain spray life. In Formulas 2911K-346 and -347 71.4 per cent sodium bisulfate powder was combined with 28.6 per cent isopropanol (91 per cent) and 28.6 per cent ethanol, respectively. In both cases the resulting rain spray life was one hour; however separation of salt and alcohol occurred after a short period of time. Formula 2911K-350 contains 71.4 per cent sodium bisulfate powder, 27.2 per cent water and 1.4 per cent Polyox WSR 205, a water soluble thickener manufactured by Union Carbide Corporation. This formulation lacks stability.

From the above results it was concluded that the most stable paste formulations giving the desired rain spray lives were those composed of sodium bisulfate and water or sodium bisulfate and ethanol or isopropanol. These formulations were found to separate after a short period of time and to date no useful additive to overcome this difficulty has been found.

With this point in mind formulations which did not contain sodium bisulfate and which were thought to be potential catalysts for the repellent formulations were investigated. Formula 2911K-334 containing 65.2 per cent titanium sulfate cake, 17.4 per cent ethylene glycol and 17.4 per cent water yielded a paste which separated after a short period of time and its use

in conjunction with Formula 2911K-291 gave a film having a negligible rain spray life. Formula 2911K-344, containing 71.4 per cent monoethanolamine sulfate and 28.6 per cent ethylene glycol, and Formula 2911K-345, containing 61.5 per cent monoethanolamine sulfate and 38.5 per cent ethanol, when used in conjunction with Formula 2911K-291, each gave repellent films having a life of five minutes. Formula 2911K-351, composed of 72.7 per cent monoethanolamine sulfate and 27.3 per cent isopropanol (91 per cent), developed a film having a 30 minute rain spray life. Formula 2911K-348, containing 61.3 per cent sulfuric acid (96 per cent), 33.3 per cent water and 5.4 per cent Cab-O-Sil, developed a film with a rain spray life of 5 minutes. Formula 2911K-349, containing 71.4 per cent aluminum sulfate hydrate and 28.6 per cent isopropanol (91 per cent), gave a film with a negligible rain spray life. Formula 2911K-352, containing 83.3 per cent p-toluene sulfonic acid and 16.7 per cent ethanol, resulted in the development of a film having a one-hour rain spray life. This formulation separated after a short period of time. Formula 2911K-353, containing 75.0 per cent p-toluene sulfonic acid and 25.0 per cent ethanol, developed a film having a rain spray life of one hour. This formulation is a saturated solution of 96 per cent p-toluene sulfonic acid ($CH_3C_6H_4SO_3H \cdot H_2O$) in ethyl alcohol. The problem of separation after a short period of time is overcome with Formula 2911K-353, as it

is a formulation consisting of only one phase, a liquid. The formulation is applied by tissue in the same manner as the paste, and as a liquid catalyst has the advantage over a paste catalyst in its ease of application.

At approximately this point in our development of a useful catalyst, a parallel investigation revealed that the repellent formulation being used lack elevated temperature storage stability. This formulation, Formula 2911K-291, contained 20 per cent dimethyldiethoxysilane, which was found to be the cause of the poor stability at elevated temperatures. Eliminating the dimethyldiethoxysilane from the formulation and replacing it with a solvent resulted in a formulation that could not be catalyzed by the sodium bisulfate paste. This formulation, Formula 2911K-290, consisting of 20 per cent Copolymer H, 20 per cent Sovasol 5, and 60 per cent Freon 12, was reevaluated with the improved p-toluene sulfonic acid catalyst. The liquid catalyst, Formula 2911K-353, when used in conjunction with repellent Formula 2911K-290, resulted in a film having a one hour rain spray life. This system has shown stability for in-flight application and stability for pre-flight application after room temperature storage for a period of one month. Formula 2911K-290 has demonstrated its stability in both applications after one month's storage at 160°F.

IV. RE-EVALUATION OF SURFACE ACTIVE AGENTS IN CONJUNCTION WITH DIMETHYLDIETHOXYSILANE

The effect of the incorporation of surface active agents on the in-flight application of acidified dimethyldiethoxysilane is reported in Interim Report No. 1, dated 27 June 1962. At that time repellents were applied to test panels under reduced rain spray conditions. Ten milliliters of repellent were sprayed through the repellent outlet of the rain spray apparatus onto the test panel in a continuous stream at a pressure of 40 psi., while the panel was exposed to a rainfall of 1 inch/hour/square foot at a wind speed of 175 miles per hour. None of the formulations tested under these conditions showed a major improvement in the overall usefulness of the repellent film. Many of the surfactants caused a greater portion of the test panel to be coated initially, but these films had decreased rain spray lives.

During the present quarter several of these formulations were re-evaluated under conditions found useful for the deposition of repellent films with silicone-titanium copolymers. Formulations which coated at least 50 per cent of the reference circle and had rain spray lives of 15 to 30 minutes under reduced rain spray were re-tested by the slow continuous release of the repellent into the windstream while the test panel was exposed to the normal test conditions of 3 inches of rainfall/hour/square foot at a wind speed of 290 miles per hour.

The following table lists the formulations which were re-evaluated. All are solutions of surface active agents in Formula 2911H-2157E, dimethyldiethoxysilane acidified with 0.25 per cent by volume sulfuric acid.

Formula 2911K-	Surfactant	Per Cent by Weight
1	Igepal CO-630	0.25
4	Arquad 2C-75	0.25
7	Nonisol 210	0.25
11	Span 85	0.25
12	Diglycol laurate	0.25
14	Span 80	0.25
28	Igepal CO-430	5.0
29	Igepal CO-430	10.0
30	Igepal CO-430	4.0

The repellents were applied to the test panel at a pressure of 5 psi. and a rate of 1 milliliter per minute for 10 minutes. It was thought that by the continuous application a durable film could be deposited, first on the periphery of the test panel and eventually over the whole panel in a manner similar to the deposition of the silicone-titanium copolymer films. Durable repellent films were formed on the area of the panel furthest from the point of impact, but continued application of the repellent did not coat the point of impact or a wide area radiating from it. The reference circle in the center of the test panel was not coated by any of the formulations tested.

V. CONCLUSIONS

Whereas combinations of Copolymer H and dimethyldiethoxysilane in aerosol packages were found to be deficient in storage stability, Copolymer H alone in aerosol containers with Freon 12 as propellent was found to be stable after one month's storage at 160°F. Copolymer H in solution in Sovasol 5 was also found to be stable.

As a catalyst for use in conjunction with Copolymer H and solutions of Copolymer H in Sovasol 5 on a dry panel in pre-flight application, a solution of 75 parts by weight of p-toluene sulfonic acid in 25 parts by weight of ethanol was found effective and stable on storage.

Re-evaluation of a number of surfactants was made in combination with acidified dimethyldiethoxysilane by a technic which comprised release at a pressure of 5 psi. at a rate of 1 milliliter per minute for 10 minutes. Repellency under rain conditions was not significantly improved.

VI. FUTURE WORK

1. Further investigation of silicone-titanium copolymers for use as a repellent both in in-flight conditions during rain and in pre-flight conditions on a dry panel.

2. Storage stability tests on rain repellent formulations.

3. Preparation of 100 kits of rain repellent considered most suitable for evaluation.

Respectfully submitted,

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VII. RESULTS OF TESTS

(Tables I and II)

Table I. - Silicone-Titanium Formulations

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
287	Silicone-Titanium Copolymer P	100.0	1 min.	100	Heavy resin formation at edges.
288	Silicone-Titanium Copolymer P	5.0	Nil	greater than 50	Resin formation at edges.
	Sovasol 4	95.0			
289	Silicone-Titanium Copolymer Q	100.0	Not tested.		
290	Silicone-Titanium Copolymer H	20.0	2 min.	100	
	Sovasol 5	20.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
291	Silicone-Titanium				
	Copolymer H	20.0	2 min.	100	
	Dimethyldiethoxysilane	20.0			
	Freon 12	60.0			
292	Silicone-Titanium				
	Copolymer H	2.0	2 min.	100	
	Sovasol 5	38.0			
	Freon 12	60.0			
293	Silicone-Titanium				
	Copolymer H	10.0	2 min.	100	
	Dimethyldiethoxysilane	10.0			
	Sovasol 5	20.0			
	Freon 12	60.0			
294	Silicone-Titanium				
	Copolymer H	4.0	2 min.	100	
	Dimethyldiethoxysilane	4.0			
	Sovasol 5	32.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life		Comments
			In-Flight	Per Cent Panel Coated	
295	Dimethyldiethoxysilane	20.0	Nil	100	Chalky film.
	Tyzor "TOG"	20.0			
	Freon 12	60.0			
296	Dimethyldiethoxysilane	10.0	Nil	100	Chalky film.
	Tyzor "TOG"	10.0			
	Sovasol 5	20.0			
	Freon 12	60.0			
297	Dimethyldiethoxysilane	20.0	Nil	100	Chalky film.
	Tyzor "TBT"	20.0			
	Freon 12	60.0			
298	Dimethyldiethoxysilane	10.0	Nil	100	Chalky film.
	Tyzor "TBT"	10.0			
	Sovasol 5	20.0			
	Freon 12	60.0			
299	Dimethyldiethoxysilane	20.0	Nil	100	Chalky film.
	Tyzor "PB"	20.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
335	Dimethyldiethoxysilane	10.0	Nil	100	Chalky film.
	Tyzor "PB"	10.0			
	Sovasol 5	20.0			
	Freon 12	60.0			
354	Silicone-Titanium Copolymer R	2.0	Nil	100	
	Dimethyldiethoxysilane	38.0			
	Freon 12	60.0			
355	Silicone-Titanium Copolymer R	4.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	36.0			
	Freon 12	60.0			
356	Silicone-Titanium Copolymer R	6.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	34.0			
	Freon 12	60.0			
357	Silicone-Titanium Copolymer R	8.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	32.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life		Comments
			In-Flight	Per Cent Panel Coated	
358	Silicone-Titanium Copolymer R	10.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	30.0			
	Freon 12	60.0			
359	Silicone-Titanium Copolymer R	12.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	28.0			
	Freon 12	60.0			
360	Silicone-Titanium Copolymer R	14.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	26.0			
	Freon 12	60.0			
361	Silicone-Titanium Copolymer R	16.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	24.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
362	Silicone-Titanium Copolymer R	18.0	1 min.	100	Hazy film.
	Dimethyldiethoxysilane	22.0			
	Freon 12	60.0			
363	Silicone-Titanium Copolymer R	4.0	2 min.	100	Poor sweep.
	Sovasol 5	36.0			
	Freon 12	60.0			
364	Silicone-Titanium Copolymer R	6.0	2 min.	100	Poor sweep.
	Sovasol 5	34.0			
	Freon 12	60.0			
365	Silicone-Titanium Copolymer R	8.0	2 min.	100	Poor sweep.
	Sovasol 5	32.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life In-Flight	Rain Spray Life Per Cent Panel Coated	Comments
366	Silicone-Titanium Copolymer R	10.0	2 min.	100	Poor sweep.
	Sovasol 5	30.0			
	Freon 12	60.0			
367	Silicone-Titanium Copolymer R	12.0	2 min.	100	Poor sweep.
	Sovasol 5	28.0			
	Freon 12	60.0			
368	Silicone-Titanium Copolymer R	14.0	2 min.	100	Poor sweep.
	Sovasol 5	26.0			
	Freon 12	60.0			
369	Silicone-Titanium Copolymer R	16.0	2 min.	100	Poor sweep.
	Sovasol 5	24.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
370	Silicone-Titanium Copolymer R	18.0	2 min.	100	Poor sweep.
	Sovasol 5	22.0			
	Freon 12	60.0			
371	Silicone-Titanium Copolymer R	40.0	2 min.	100	Poor sweep. Resinous formation.
	Freon 12	60.0			
372	Silicone-Titanium Copolymer R	20.0	1 min.	100	Heavy resinous formation.
	Methyl Silicone Oil 100 cs.	20.0			
	Freon 12	60.0			
373	Silicone-Titanium Copolymer R	10.0	1 min.	100	Heavy resinous formation.
	Methyl Silicone Oil 100 cs.	30.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
374	Silicone-Titanium Copolymer R	20.0	1 min.	100	Poor sweep.
	Dimethyldiethoxysilane hydrolysate	20.0			
	Freon 12	60.0			
375	Silicone-Titanium Copolymer R	20.0	1 min.	100	Heavy resinous formation.
	Methyl Silicone Oil 10 cs.	20.0			
	Freon 12	60.0			
376	Silicone-Titanium Copolymer R	20.0	1 min.	100	Resinous formation. Poor sweep.
	Dimethyldiethoxysilane	20.0			
	Freon 12	60.0			
377	Silicone-Titanium Copolymer R	2.0	2 min.	100	
	Sovasol 5	38.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life		Comments
			In-Flight	Per Cent Panel Coated	
378	Silicone-Titanium Copolymer R	20.0	2 min.	100	Poor sweep.
	Sovasol 5	20.0			
	Freon 12	60.0			
379	Silicone-Titanium Copolymer H	40.0	2 min.	100	Fair sweep.
	Freon 12	60.0			
380	Silicone-Titanium Copolymer S	20.0	1 min.	100	Poor sweep.
	Sovasol 5	20.0			
	Freon 12	60.0			
381	Silicone-Titanium Copolymer H	4.0	2 min.	100	Good sweep.
	Sovasol 5	36.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
382	Silicone-Titanium Copolymer H	6.0	2 min.	100	Good sweep.
	Sovasol 5	34.0			
	Freon 12	60.0			
383	Silicone-Titanium Copolymer H	8.0	2 min.	100	Good sweep.
	Sovasol 5	32.0			
	Freon 12	60.0			
384	Silicone-Titanium Copolymer H	10.0	2 min.	100	Good sweep.
	Sovasol 5	30.0			
	Freon 12	60.0			
385	Silicone-Titanium Copolymer H	12.0	2 min.	100	Good sweep.
	Sovasol 5	28.0			
	Freon 12	60.0			
386	Silicone-Titanium Copolymer H	14.0	2 min.	100	Good sweep.
	Sovasol 5	26.0			
	Freon 12	60.0			

Table I. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Volume	Rain Spray Life: In-Flight	Rain Spray Life: Per Cent Panel Coated	Comments
387	Silicone-Titanium Copolymer H	16.0	2 min.	100	Good sweep.
	Sovasol 5	24.0			
	Freon 12	60.0			
388	Silicone-Titanium Copolymer H	18.0	2 min.	100	Good sweep.
	Sovasol 5	22.0			
	Freon 12	60.0			
389	Silicone-Titanium Copolymer H	20.0	2 min.	100	Fair sweep.
	n-Butanol	20.0			
	Freon 12	60.0			
390	Silicone-Titanium Copolymer H	20.0	2 min.	100	Fair sweep.
	Isopropanol 99%	20.0			
	Freon 12	60.0			

Table II. Catalysts for Pre-Flight Application

Formula No. 2911K-	Composition	Per Cent by Weight	Applicator	Rain Spray Life	Comments
334	Titanium sulfate	65.2	Tissue	Nil	Paste separates.
	Ethylene glycol	17.4			
	Water	17.4			
336	Sodium bisulfate - crystal	71.4	Tissue	15 min.	
	Ethylene glycol	28.6			
337	Sodium bisulfate - powder	71.4	Tissue	15 min.	
	Ethylene glycol	28.6			
338	Sodium bisulfate - powder	71.4	Tissue	15 min.	
	Ethylene glycol	25.7			
	Water	2.9			
339	Sodium bisulfate - crystal	71.4	Tissue	---	Paste is unstable.
	Hexylene glycol	28.6			
340	Sodium bisulfate - powder	62.5	Tissue	---	Paste is unstable.
	Hexylene glycol	37.5			
341	Sodium bisulfate - powder	57.1	Tissue	Nil	
	Methyl Silicone Oil - 200 cs.	42.9			

Table II. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Weight	Applicator	Rain Spray Life	Comments
342	Sodium bisulfate - powder Water	71.4 28.6	Tissue	1 hr.	
343	Sodium bisulfate - crystal Ethylene glycol Water	71.4 17.9 10.7	Tissue	30 min.	Paste separates.
344	Monoethanolamine sulfate Ethylene glycol	71.4 28.6	Tissue	5 min.	
345	Monoethanolamine sulfate Ethanol	61.5 38.5	Tissue	5 min.	
346	Sodium bisulfate - powder Isopropanol, 91%	71.4 28.6	Tissue	1 hr.	
347	Sodium bisulfate - powder Ethanol	71.4 28.6	Tissue	1 hr.	
348	Sulfuric acid, 96% Water Cab-O-Sil	61.3 33.3 5.4	Tissue	5 min.	

Table II. (Cont'd.)

Formula No. 2911K-	Composition	Per Cent by Weight	Applicator	Rain Spray Life	Comments
349	Aluminum sulfate hydrate Isopropanol, 91%	71.4 28.6	Tissue	Nil	
350	Sodium bisulfate - powder Water Polyox WSR-205	71.4 27.2 1.4	Tissue	---	Paste is unstable.
351	Monoethanolamine sulfate Isopropanol, 91%	72.7 27.3	Tissue	30 min.	
352	p-Toluene sulfonic acid Ethanol	83.3 16.7	Tissue	1 hr.	Paste separates.
353	p-Toluene sulfonic acid Ethanol	75.0 25.0	Tissue	1 hr.	Liquid.